Beryllium Limits of Detection and Spectral Interferences in 2% Nitric Acid, Digested Air Filter Paper, and GHOSTWIPE™Matrices by Inductively Coupled Plasma Emission Spectrometry (U)

December 15, 2003

Savannah River Technology Center
Measurement Technology Department
Analytical Development Section

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

Keywords:
Beryllium
LOD
Interference
ICP-ES
Filter
Retention:
Lifetime

Beryllium Limits of Detection and Spectral Interferences in 2% Nitric Acid, Digested Air Filter Paper, and GHOSTWIPE™ Matrices by Inductively Coupled Plasma Emission Spectrometry

A. R. Jurgensen
J. C. Hart
L. L. Farrow

December 15, 2003

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ACRONYMS

ADS	Analytical Development Section
Be	Beryllium
IH	Industrial Hygiene
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of Detection
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Science and Technology
SRTC	Savannah River Technology Center
WSRC	Westinghouse Savannah River Company

Introduction

The Analytical Development Section (ADS) of the Savannah River Technology Center (SRTC) has been requested to perform beryllium (Be) analysis on digested Air Filter Paper and GHOSTWIPE™ samples by Inductively Coupled Plasma Emission Spectrometry (ICP-ES). One of the important figures of merit for this analysis is the detection limit (LOD), the smallest concentration of an element that can be detected with a defined certainty. To meet the site Industrial Hygiene (IH) requirements, an instrument LOD of 0.03 μg per Air Filter Paper (1hr sample) and 0.2 μg per GHOSTWIPE™ must be demonstrated. Another important analytical parameter is the effect on the Be quantitation from potential spectral interfering matrix elements. Any existing spectral overlaps could give false positives or increase the measured Be concentrations in these matrices. The purpose of this study was to document the Analytical Development Sections' s contained ICP-ES performance in these two areas. In addition, other Quality Control recommendations will be discussed.

Experimental

Limits of Detection have been determined utilizing the International Union of Pure and Applied Chemistry (IUPAC)[1] methodology as follows:

$$X_L = \overline{X}_{bl} + ks_{bl}$$

$$C_L = (X_L - \overline{X}_{bl})/S$$

where

X_L: Smallest measure detected with reasonable certainty
$\overline{X}_{bl}$: Mean of blank measures
k: Uncertainty factor
s_{bl}: Standard deviation of blank measures
C_L: Limit of Detection
S: Sensitivity (Slope of the Calibration Curve)

Note: "A value of 3 for k . . . is strongly recommended; for this value, a 99.6% confidence level applies only for a strictly one sided Gaussian distribution. At low concentrations, non-Gaussian distributions are more likely. Moreover, the values of $\overline{X}_{bl}$ and S_{bl} are themselves only estimates based on limited measurements. Therefore, in a practical sense, the 3 S_{bl} value usually corresponds to a confidence level of about 90%." [1] ADS has chosen to use k = 5 to increase the confidence interval above 90%.

---

[1] IUPAC Compendium of Analytical Nomenclature, Definitive Rules, 3rd Edition, Section 10.3.3.3.1 "Limit of Detection" (1997).

The instrument used for these measurements is a Horiba Jobin Yvon Model 170C Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-ES) with a 1.5 kW, 40 MHz solid-state generator and torch box assembly contained in a radiological fume hood[2]. The spectrometer section of the instrument consists of a 1-meter Czerny-Turner monochromator with a 1-m focal length , 80 x 110 mm, 2400 grooves/mm grating with 7 pm resolution (2nd order full width half max) at 234 nm and 12 pm resolution (1st order full width half max) at 313 nm and a 0.5-meter polychromator. The polychromator uses a Paschen-Rungen (Rowland Circle) design with a 0.5-m focal length (3000 grooves/mm) grating in first order and with a flat-field segment to detect Na, Li and K. All measurements were made in the Gaussian peak mode, with nine points sampled across the Be emission line peak shape. Although lower LODs could be acquired in the single or "median" (5 points) modes, the Gaussian mode provides higher precision data, since more points on the emission profile are measured. In addition, there is acceleration in the calibration curve drift in the single or "median" modes. All data were acquired following procedure ADS-1564, "Contained ICP-ES for Radioactive Sample Analysis, JY170C". The Be measurements were made sequentially on the monchromator since there were no Be channels on the polychromator, the simultaneous portion of the unit. A 2 μg/mL Sc internal standard was added to all solutions to compensate for minor fluctuations in the plasma and sample introduction system. Scandium intensity was measured simultaneous to beryllium using a fixed channel on the polychromator.

GHOSTWIPES™ and Air Filter Paper blanks were dissolved in HNO_3 and HF following the IH modified NIOSH 7300 procedure, "Elements by ICP". Due to solubility issues the final solution volumes were limited to 25 mL for the GHOSTWIPE™ and only 10 mL for the Air Filter Paper. For the LOD determination twenty replicate blank measurements of the 2% nitric acid solution were collected while only ten blank replicates were obtained for the Air Filter and GHOSTWIPE™ matrices due to a limited supply of matrix blank solution. The number of replicate blank measurements is not specified by IUPAC for the LOD determination, but in the literature the recommended value is twenty[3,4]. The Be sensitivity (slope of the calibration curve) was calculated from the intensities of the matrix blank, a 2 μg/mL, and a 5 μg/mL Be standard solution. The standards were made from a 1000 μg/mL NIST traceable stock solution diluted in the appropriate matrix blank.

For the spectral interference study, three 100 μg/mL mixed standards and several high concentration single element standards were analyzed on all four Be lines to determine the equivalent Be detected in μg/mL in HNO_3 and in μg per Air Filter Paper and GHOSTWIPE™. As for the LOD study, all the standards were diluted from a 1000 μg/mL NIST traceable stock solution and spiked with 2 μg/mL Sc added as an internal standard. To eliminate carry-over, a 2% HNO_3 solution was flushed through the system

---

[2] F.M. Pennebaker and J.C. Hart, WSRC-TR-2003-00063, "Final Report on Jobin Yvon Contained Inductively Coupled Plasma Emission Spectrometer (ICP-ES)".

[3] P. W. J. M Boumans, Inductively Coupled Plasma Emission Spectroscopy, Part 1, Methodology, Instrumentation, and Performance, (John Wiley & Sons, New York ,1987), p 106.

[4] J. D. Winefordner, Trace Analysis, Spectroscopic Methods for Elements, (John Wiley & Sons, New York, 1976), p 5.

between interferent solutions until the background intensity was reduced to the blank level.

Results and Discussion

The Be LOD results on a solution and mass / swipe basis are listed in Tables 1 and 2, respectively. The IH required LOD is met by three of the four beryllium lines. Only the Be 265.015 nm emission line has an LOD in Air Filter matrix that is above the acceptable level. The LODs for the other three lines are very similar and 5 – 20x lower than the IH limit. What's interesting is that the matrix had statistically no discernible effect on the LODs in solution. The differences are probably more related to daily instrument fluctuations and not due to matrix effects. Detailed intensity data used for these calculations in all three matrices are listed in Tables 3, 4, & 5.

The spectral interferences on all four Be emission lines in μg/mL in 2% HNO_3, μg/Air filter Paper, and μg/ GHOSTWIPE™ are listed in Tables 6, 7, and 8. The interferences are considerably lower on the 234 line than the other lines and non-existent at matrix element concentrations < 90 ppm. The only element that could be a real problem for this wavelength, Fe, doesn't interfere with the two 313 lines. Note, in no case does the interference factor by a matrix element on the 234 and 313 lines result in identical instrument response. These factors differ by ~ 10x. If the 234 and 313 Be values are the same, there are no spectral interferences or they are insignificant. It is possible, except in the unlikely case of very high interferent concentrations, by judicious line selection to completely avoid any spectral interference corrections.

Methodology

The following is a summary of the ADS ICP methodology currently being used:

- If the sample volume is an issue, eliminate the 265.015 nm wavelength from the Be method. It had the poorest LOD and is very prone to spectral interferences. The analysis time will be reduced by 25% by removing this line. That still leaves three lines for the determination.
- If needed for filter paper samples where there is only 10 mL of solution available for analysis, eliminate one of the 313 lines. They behave like "identical twins" with the same LODs and spectral interferences. Removing one of these lines will reduce the analysis time by an additional 25% and more importantly leave more residual sample for further analysis.
- Use the 234 emission line for the Be LOD when there is no evidence that it is biased by spectral overlaps, particularly for Fe, or suppression. This level is the most conservative of the three and the 234 line doesn't suffer to the same degree from matrix effects as the other two. It's important that we don't report a false positive.
- For each sample with a positive Be value perform a routine ICP scan to identify any potential interferents. If the values for the 234 and 313 lines are statistically

different, identify the reason for the discrepancy[5]. If possible, try to avoid using any spectral interference correction factors. Use of a spectral interference correction factor adds an additional degree of uncertainty to the determination. The 234 line is less likely to be affected by any matrix interferences (except for Fe) and should be used whenever possible. If the concentrations on all lines are the same, it is highly unlikely that there are any matrix issues. To ensure confidence an analysis for the full routine element suite will be completed.

- If Be is determined to be present, the average of all the appropriate lines will be used as the reportable Be concentration. This should improve its accuracy. It would be similar to analyzing the sample multiple times on one line. Report only this average value for each sample, after peer review, to the customer in a summary sheet.
- Analyze a matrix or Laboratory Control Blank (LCB) at the beginning of each batch of samples to verify that no contaminants are being introduced during the digestion process and in between samples to demonstrate that the sample introduction apparatus was properly flushed and the intercept of the calibration curve has not drifted.
- Analyze a Laboratory Control Standard (LCS) at or near the IH limit at the beginning and end of each batch of samples. Currently, only filter papers spiked with 0.1 and 0.2 μg of Be are available from High Purity Standards. The determined beryllium concentration for each LCS should be within +/- 25% deviation from the known value. If not the method, the digestion and/or ICP-ES analysis, is out of control and the data set associated with that QC standard is invalid unless otherwise qualified by IH.
- Measure an LOD check standard (10 ng/mL Be) with each batch of samples.
- Re-measure the LODs and reassess potential spectral interferences every six months or after any major maintenance that could affect the instrument sensitivity or resolution. The sensitivity, particularly the 234 line, will steadily decrease as the lens coupling the atomic emission to the monochromater is subjected to “UV burn”.

---

[5] It is critical in the identification of potential interferences that the customer identify elements that may be present in their sample. If the suspected interferents are not in our “routine” analysis list, additional investigation will be required.

Table 1. Be Limits of Detection in Solution.

	IUPAC 5σ LOD (μg/mL)			
Matrix	**Be234.861**	**Be265.015**	**Be313.042**	**Be313.107**
2% HNO_3	0.001	0.009	0.001	0.0007
Filter Paper	0.0007	0.005	0.0007	0.0006
GHOSTWIPE™	0.0005	0.007	0.0002	0.0003

Table 2. Be Limits of Detection (μg Be/Filter Paper or GHOSTWIPE™).

	IUPAC 5σ LOD (μg/Filter or GHOSTWIPE™)			
Matrix	**Be234.861**	**Be265.015**	**Be313.042**	**Be313.107**
Filter Paper	0.008	0.06	0.007	0.007
GHOSTWIPE™	0.01	0.2	0.005	0.007

Filter Paper IH Limit: 0.03 μg – for a 1 hr sample
GHOSTWIPE™ IH Limit: 0.2 μg

Table 3. Limits of Detection for Be in a 2% HNO_3 matrix.

	Raw Peak Intensity / Sc Int. Std. Intensity			
	Be234.861	**Be265.015**	**Be313.042**	**Be313.107**
Blank1	0.00711	0.0126	0.0153	0.0156
Blank2	0.00697	0.0129	0.0156	0.0156
Blank3	0.00688	0.0131	0.0159	0.0160
Blank4	0.00706	0.0127	0.0153	0.0150
Blank5	0.00722	0.0125	0.0153	0.0155
Blank6	0.00708	0.0132	0.0159	0.0156
Blank7	0.00719	0.0130	0.0153	0.0159
Blank8	0.00715	0.0125	0.0159	0.0158
Blank9	0.00709	0.0119	0.0154	0.0154
Blank10	0.00712	0.0121	0.0152	0.0155
Blank11	0.00684	0.0133	0.0155	0.0154
Blank12	0.00710	0.0124	0.0155	0.0152
Blank13	0.00716	0.0132	0.0156	0.0159
Blank14	0.00712	0.0127	0.0157	0.0155
Blank15	0.00739	0.0128	0.0160	0.0161
Blank16	0.00690	0.0127	0.0157	0.0160
Blank17	0.00867	0.0123	0.0170	0.0161
Blank18	0.00812	0.0128	0.0162	0.0162
Blank19	0.00750	0.0125	0.0166	0.0159
Blank20	0.00792	0.0124	0.0159	0.0157
Blank Avg.	0.00728	0.0127	0.0157	0.0157
Blank Stdev.	0.00046	0.00037	0.00046	0.00032
2 μg/mL Be	4.19	0.42	4.13	4.14
5 μg/mL Be	10.60	1.05	10.98	10.74
S (Intensity/(μg/mL))	2.120	0.2078	2.200	2.149
IUPAC 3σ LOD (μg/mL)	0.0006	0.005	0.0006	0.0004
IUPAC 5σ LOD (μg/mL)	0.001	0.009	0.001	0.0007

Table 4. Limits of Detection for Be in a Dissolved Air Filter Matrix.

	Raw Peak Intensity / Sc Int. Std. Intensity			
	Be234.861	**Be265.015**	**Be313.042**	**Be313.107**
Blank1	0.00943	0.0149	0.0182	0.0174
Blank2	0.00881	0.0151	0.0179	0.0178
Blank3	0.00880	0.0153	0.0175	0.0176
Blank4	0.00859	0.0146	0.0172	0.0176
Blank5	0.00880	0.0152	0.0177	0.0174
Blank6	0.00854	0.0152	0.0177	0.0172
Blank7	0.00865	0.0150	0.0176	0.0176
Blank8	0.00840	0.0150	0.0175	0.0177
Blank9	0.00841	0.0152	0.0178	0.0183
Blank10	0.00845	0.0152	0.0183	0.0178
Blank Avg.	0.00869	0.01507	0.01774	0.01764
Blank Sdev.	0.00031	0.00021	0.00033	0.00030
2 μg/mL Be	4.18	0.43	5.02	5.02
5 μg/mL Be	10.30	1.02	12.28	12.13
S (Intensity/(μg/mL))	2.0568	0.2007	2.4499	2.4183
IUPAC 3σ LOD (μg/mL)	0.0004	0.003	0.0004	0.0004
IUPAC 5σ LOD (μg/mL)	0.0007	0.0051	0.0007	0.0006

Table 5. Limits of Detection for Be in a Dissolved GHOSTWIPE™ Matrix.

	Raw Peak Intensity / Sc Int. Std. Intensity			
	Be234.861	**Be265.045**	**Be313.042**	**Be313.107**
Blank1	0.00844	0.0130	0.0163	0.0159
Blank2	0.00797	0.0134	0.0160	0.0162
Blank3	0.00841	0.0133	0.0161	0.0161
Blank4	0.00832	0.0134	0.0160	0.0162
Blank5	0.00811	0.0129	0.0161	0.0158
Blank6	0.00811	0.0138	0.0161	0.0160
Blank7	0.00813	0.0134	0.0159	0.0159
Blank8	0.00792	0.0135	0.0160	0.0158
Blank9	0.00796	0.0134	0.0160	0.0161
Blank10	0.00807	0.0139	0.0160	0.0160
Blank Avg.	0.00814	0.01340	0.01605	0.01600
Blank Stdev.	0.00019	0.00031	0.00011	0.00015
2 μg/mL Be	4.23	0.45	5.71	5.66
5 μg/mL Be	10.35	1.07	13.97	14.03
S (Intensity/(μg/mL))	2.0661	0.2111	2.7878	2.8018
IUPAC 3σ LOD (μg/mL)	0.0003	0.004	0.0001	0.0002
IUPAC 5σ LOD (μg/mL)	0.0005	0.007	0.0002	0.0003

Table 6. Equivalent Be (µg/ml) in 2% HNO_3 Matrix

	Be234.861	Be265.015	Be313.042	Be313.107
[1]Mix A - 100 µg/ml	<0.001	0.11	0.007	0.007
[2]Mix B - 100 µg/ml	<0.001	0.041	0.017	0.017
[3]Mix C - 100 µg/ml	<0.001	0.011	<0.001	<0.0007
Al - 300 µg/ml	<0.001	0.022	<0.001	<0.0007
Ce - 100 µg/ml	<0.001	0.009	<0.001	<0.0007
Cr - 900 µg/ml	<0.001	0.044	0.006	0.006
Cu - 900 µg/ml	<0.001	<0.009	<0.001	<0.0007
Er - 900 µg/ml	0.003	0.32	0.74	0.75
Fe - 900 µg/ml	0.010	0.064	<0.001	<0.0007
Gd - 100 µg/ml	<0.001	<0.009	<0.001	<0.0007
Mo - 900 µg/ml	0.001	0.715	0.007	0.007
Nb - 900 µg/ml	0.0096	0.273	0.087	0.088
Ni - 900 µg/ml	<0.001	0.16	<0.001	<0.0007
Pu - 963 µg/ml	0.002	0.27	0.009	0.014
Th - 986 µg/ml	<0.001	90	0.70	0.70
Ti - 900 µg/ml	0.001	0.034	0.011	0.011
U - 900 µg/ml	0.005	0.95	0.068	0.070
V - 900 µg/ml	<0.001	0.13	0.010	0.010
Zr - 900 µg/ml	0.006	0.092	0.13	0.13

[1] Mix A = Al, Ba, Ca, Ce, Cr, Fe, Gd, K (250), La, Li, Mg, Mn, Na, Ni, Pb, Sr, U
[2] Mix B = Ag, Cd, Cu, Mo, Sb, Sn, Ti, V, Zn, Zr
[3] Mix C = B, P, S, Si

Table 7. Equivalent Be (µg/Air Filter Paper).

	Be234.861	Be265.015	Be313.042	Be313.107
[1]Mix A - 100 µg/ml	<0.008	1.2	0.077	0.077
[2]Mix B - 100 µg/ml	<0.008	0.45	0.19	0.19
[3]Mix C - 100 µg/ml	<0.008	0.12	<0.007	<0.007
Al - 300 µg/ml	<0.008	0.24	<0.007	<0.007
Ce - 100 µg/ml	<0.008	0.099	<0.007	<0.007
Cr - 900 µg/ml	<0.008	0.48	0.066	0.066
Cu - 900 µg/ml	<0.008	<0.06	<0.007	<0.007
Er - 900 µg/ml	0.033	3.5	8.1	8.3
Fe - 900 µg/ml	0.11	0.70	<0.007	<0.007
Gd - 100 µg/ml	<0.008	<0.06	<0.007	<0.007
Mo - 900 µg/ml	0.011	7.9	0.077	0.077
Nb - 900 µg/ml	0.106	3.0	1.0	1.0
Ni - 900 µg/ml	<0.008	1.8	<0.007	<0.007
Pu - 963 µg/ml	0.022	2.9	0.099	0.15
Th - 986 µg/ml	<0.008	990	7.7	7.7
Ti - 900 µg/ml	0.011	0.37	0.12	0.12
U - 900 µg/ml	0.055	10	0.75	0.77
V - 900 µg/ml	<0.008	1.4	0.11	0.11
Zr - 900 µg/ml	0.066	1.0	1.4	1.4

[1] Mix A = Al, Ba, Ca, Ce, Cr, Fe, Gd, K (250), La, Li, Mg, Mn, Na, Ni, Pb, Sr, U
[2] Mix B = Ag, Cd, Cu, Mo, Sb, Sn, Ti, V, Zn, Zr
[3] Mix C = B, P, S, Si

Table 8. Equivalent Be (µg/GHOSTWIPE™).

	Be234.861	**Be265.015**	**Be313.042**	**Be313.107**
[1]Mix A - 100 µg/ml	<0.01	2.9	0.19	0.19
[2]Mix B - 100 µg/ml	<0.01	1.1	0.47	0.47
[3]Mix C - 100 µg/ml	<0.01	0.30	<0.005	<0.007
Al - 300 µg/ml	<0.01	0.61	<0.005	<0.007
Ce - 100 µg/ml	<0.01	0.25	<0.005	<0.007
Cr - 900 µg/ml	<0.01	1.2	0.17	0.17
Cu - 900 µg/ml	<0.01	<0.2	<0.005	<0.007
Er - 900 µg/ml	0.083	8.7	20	21
Fe - 900 µg/ml	0.28	1.8	<0.005	<0.007
Gd - 100 µg/ml	<0.01	<0.2	<0.005	<0.007
Mo - 900 µg/ml	0.028	20	0.19	0.19
Nb - 900 µg/ml	0.26	7.5	2.4	2.4
Ni - 900 µg/ml	<0.01	4.4	<0.005	<0.007
Pu - 963 µg/ml	0.055	7.3	0.25	0.39
Th - 986 µg/ml	<0.01	2475	19	19
Ti - 900 µg/ml	0.028	0.94	0.30	0.30
U - 900 µg/ml	0.14	26	1.9	1.9
V - 900 µg/ml	<0.01	3.5	0.28	0.28
Zr - 900 µg/ml	0.17	2.5	3.6	3.6

[1] Mix A = Al, Ba, Ca, Ce, Cr, Fe, Gd, K (250), La, Li, Mg, Mn, Na, Ni, Pb, Sr, U
[2] Mix B = Ag, Cd, Cu, Mo, Sb, Sn, Ti, V, Zn, Zr
[3] Mix C = B, P, S, Si